ment of ES probe tips **173**, **174** and **175** respectively as was previously described for the ES probe assemblies **120** and **122** in **FIG. 6**. In the embodiment shown in **FIG. 8**, the x-y-z and angular position of ES probe tips **173**, **174** and **175** can be adjusted during tuning of Electrospray source performance. Each ES probe tip position can be adjusted to optimize ES-MS or ES-MS/MS_n performance during single or simultaneous multiple probe operation for a wide range of combinations of liquid flow rates and solution compositions.

[**0060**] Once the positions of ES probe tips **173**, **174** and **175** are optimized during ES-MS operation tuning, no further adjustment is required during ES source operation and MS data acquisition. ES probe assemblies **170** and **172** are each configured with three layer ES probe tips **173** and **175** respectively as is shown in **FIG. 13**. ES probe assembly **171** is configured with two layer ES tip **174** as is shown in **FIG. 12**. Solution can be Electrosprayed from ES probe assemblies **173** and **175** with or without pneumatic nebulization assist and/or liquid layer flow. The positions of ES tips **173**, **174** and **175** are, Z_{173}, R_{173}, Z_{175}, R_{175} and Z_{174} respectively with ES tips **173** and **175** set spray angles of ϕ_{173} and ϕ_{175}, and radial angles θ_{173} and θ_{175}, respectively. As examples shown in **FIG. 8**, ES probe tip **173** is set at an angle of +60 degrees (ϕ_{173}=+60°) and ES probe tip **175** is set at an angle of −60 degrees (ϕ_{175}=−60° or +300 degrees) relative to ES source centerline **177**. The included angle, (ϕ_{173}-ϕ_{175}), between ES probe tips **173** and **175** in the embodiment shown is 120 degrees, however, this included angle can vary from zero degrees to 180 degrees. The relative radial angle of separation between ES probe tips **173** and **175** (θ_{173}-θ_{175}) equals 180 degrees. ES probe tip **174** is positioned with its axis falling on ES source centerline **177**. The relative angle between either ES probe tip **173** or **175** and ES probe tip **174** is 60 degrees. The relative angles between all ES tips probes mounted simultaneously in ES source chamber **161** can vary from close to zero to over 180 degrees depending on the analytical application being run. The radial probe separation can range from 0 to 360 degrees. Multiple ES probes can alternatively be mounted on ES source back plate **179** as is shown in **FIG. 1** or through the side walls of ES chamber **161** as shown in **FIG. 8**, each with fixed positions or individual position adjusters. One or more ES probes can be mounted on the back plate as shown in **FIG. 1** or ES probe assemblies mounted on back plate **178** may be configured with one or more ES probe assemblies which extend through a side wall or walls of ES chamber **161** as shown in **FIG. 8**.

[**0061**] A portion of the ions produced from the simultaneous Electrospraying of solutions from at least two of ES probes tips **173**, **174** and/or **175** are swept into vacuum, through capillary orifice **164**, where they are mass analyzed. With the appropriate liquid delivery systems, the solution flow to ES probe tips **173**, **174** or **175** can be turned on or off independent of the layered liquid flow or nebulizer gas flow supplied to any given ES probe tip. For example, Electrospray from ES probe tip **173** can be turned off if the sample liquid flow through line **179** to ES probe assembly **170** were tuned off independent of whether the sample liquid flow through line **180** to ES probe assembly **172** remains on. The nebulizer gas flow to ES probe assembly **170** supplies through line **180** can remain on independent of the sample solution flow status through line **178**. Leaving the nebulizer gas flow on, even with solution flow through ES probe **170** turned off, retains the optimal drying gas flow characteristics in ion mixing region **182** where the nebulization gas from ES probes and ES source counter current gas flow **183** meet. After the gas flow balance into region **182** has been optimized, the gas flow into this region can remain constant even when sample flow is introduced through one or more ES probes individually or simultaneously. Optimal ES-MS performance can be achieved when multiple nebulization gas flows remain on even with combinations of sample flows being turned on an off independently through multiple ES probe tips. Alternatively, the gas and liquid flow supplied to ES probe tip **175** can be alternately switched on when the gas and liquid flow supplied to ES probe tip **173** is turned off. The liquid and gas flow through ES tip **174** can remain ion while spraying sample solution from either ES probe tips **173** or **175**. In the embodiment diagrammed in **FIG. 8**, ES probe tips **173** and **175** are located in a positions that are radially symmetric relative to the position of ES probe tip **174**. Gas flow through ES probe tips **173** and **175** can be adjusted to be symmetric and equal in mixing region **182** when the liquid and gas flows to ES probe tips **173** and **175** are switched on and off in an alternating manner. The relative positions of each probe can also be adjusted so that performance is optimized different liquid flow rates are delivered through ES probe tips **173** and **175**. In the case of alternating Electrospraying through ES probe tips **173** and **175**, calibration solution can be delivered through ES probe **174** to provide an internal standard in the acquired mass spectrum when spraying individually or simultaneously from ES probe tips **173** and **175**. When a heated capillary is configured in API source, heated counter current gas flow **183** may or may not be required. Partially evaporated charged liquid droplets swept into a heated capillary evaporate further on the way to vacuum. Ions produced from multiple solution sources, mix in partial vacuum or in vacuum prior to mass analysis. Ion mixtures may be formed by trapping ions produced from different Electrospray probes in three dimensional ion traps or multipole ion guides operated as two dimensional ion traps in vacuum as well. Mixtures of ions in three and two dimensional ion can be formed by trapping ions formed from simultaneous or individual sequential Electrospraying from multiple ES probes.

[**0062**] Individual separation systems such as LC, CE or CEC can serve as the solution delivery systems to different ES probes configured in an ES chamber. Multiple ES probes configured in an Electrospray ion source allow a single ES mass spectrometer system to serve as a detector for multiple separation systems without the need to switch eluting samples through a common probe. A common ES probe may not be optimally configured or even compatible for each separation system configured with the ES source. Multiple ES probes avoids cross contamination from one sample injection to the next delivered from individual separate systems. The separation of compounds spatially in solution is generally the slow step of an LC, CE or CEC MS analytical analysis, particularly when a mass spectrometer capable of rapid data acquisition, such as Time-Of-Flight, is used. The use of multiple ES probes combined with efficient manual or automated sample introduction increases analytical throughput with no risk of performance loss due sample cross contamination. The mass spectrometer, configured to operate in MS or MS^n mode with multiple separation systems, can serve as a detector for a wide range of chemical analysis run in a manual or automated mode without the